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CERAMIC ELASTICALLY STIFF AND ELASTICALLY RESILIENT SEMIPERMEABLE MEMBRANES

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The results of obtaining ceramic elastically stiff and elastically resilient capillary-porous structures are presented, and the possibility of modifying them into thin-layer semi-permeable membranes with filtration properties is investigated. It is determined that the most effective technological methods for fabricating ceramic membranes based on spondilovaya clay and calcium-phosphate materials are semi-dry multistep pressing of the initial powders and casting from suspensions. A comparative investigation of the elastically stiff membranes consisting of two basic compositions is performed, and it is established that a capillary-porous structure is present and that the values of their gas permeability and the rate of filtration are close. The investigation of elastically resilient resorbable and semi-resorbable membranes based on biogenic hydroxyapatite showed that these materials have promise for applications in medicine.

Ceramics with capillary-porous structure in the form of diaphragms and membranes are systems with an internal interphase surface, which makes it possible to use them to separate colloidal dispersions on the basis of the properties of porous structures to selectively pass certain materials.

Membranes are distinguished by the transfer mechanism for the passing material, are divided into diffusion, electric, and hydrodynamic, and in individual cases are used together to accelerate steady mass transfer or improve the separation of solution components. In addition, membranes are classified as filtration and diffusion membranes according to indicators associated with the equilibrium or kinetic properties of the system being separated. Semi-permeable filtration barriers in the form of films or plates, possessing a large specific internal surface area, are capable of separating substances under equilibrium conditions because their pores are comparable in size to the penetrating particles or high-molecular compounds [1].

Filtration membranes are classified as macroporous, intermediate-porous, and microporous, similarly to adsorbents with porous channel radii in the ranges ≥ 200, 2 – 200, and 0.5 – 2.0 nm, respectively. They possess more or less stiff spatial networks or frameworks, different degrees of brittleness, selectivity, and adsorption power with respect to moisture [1].

Ceramic semi-permeable membranes must possess a definite mechanical strength and be distinguished by the uniformity of the density distribution, which is a very important criterion for choosing a method for forming ceramic parts. The main specific characteristic of capillary-porous structures is their permeability, equally important for filtration membranes intended for separation or selective extraction and purification of substances as well as for biological membranes for use in medical practice as a biocompatible ion-exchange mechanical barrier or osteoconductive material for filling defects in bone tissue [2]. Calcium-phosphate materials with particle size 40 – 160 μm are most often used in jaw-facial and stomatological surgery and orthopedics for filling bone defects. It is necessary to use biological membranes to prevent "washing out" of separate particles from the zone of periodontal or other bone defect. This biocompatible mechanical barrier prevents apical migration of gum epithelia or connective tissues and delivers calcium and phosphorus ions for regeneration of the bone tissue in the zone of the defect.

The present work considers the questions of obtained and investigating filtration ceramics based on spondilovaya clay as a model material and hydroxyapatite $Ca_{10-x}(PO_4)_6(OH)_2$ of synthetic and biogenic origin (SHAp and BHAp). The objective was to study the possibility of creating semi-perme-

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TABLE 1.

Membranes	Material for fabrication	Final composition of the matrix	Mass content of components, %	Membrane thickness, mm	Production technology	Purpose
Elastically stiff:						
UZhM-1	Hydroalumino-silicates	Spondilovaya clay	100	2.0 – 4.0	Plastic + semi-dry pressing, calcination	Filtration purification
UZhM-1m (modified)	″	Clay + highly dispersed bentonite coating	100	2.0 – 4.0	Semi-dry pressing, calcination, colmatage with bentonite, calcination	Same
UZhM-2	Synthetic calcium phosphate + hydroxyapatite	Calcium phosphate + bentonite	60 + 40	1.5 – 2.0	Semi-dry pressing, calcination	″
Elastically resilient:						
UÉM-1	Biogenic hydroxy-apatite + PVA	BHp + polymer	From 80 + 20 to 90 + 10	0.5 – 2.0	Slip casting, drying	Stomatological membranes
UÉM-2	BHAp + sodium-silicate glass + PVA	Glass-modified BHAp + polymer	80 + 20	0.4 – 1.5	Same	Same

able non-calcined and calcined structures with uniform density and the properties of filtration membranes.

The chemical composition of the spondilovaya clay was as follows (%[2]): 59.90 – 60.0 SiO_2, 12.10 – 12.20 Al_2O_3, 4.61 Fe_2O_3, 10.36 CaO, 1.18 MgO, 0.53 – 0.56 ($K_2O + Na_2O$), ≤ 0.40 SO_3, 10.60 calcination losses. Before being put to use, the clay was dried to a constant mass at 150°C and comminuted in a ball mill, and the initial powders with particle size ≤ 50 μm were obtained.

The sol-gel technology was used to obtain synthetic calcium-phosphate materials by the method of chemical precipitation in an alkaline medium [2]. The precipitated gel was dried at 70 ± 5°C and calcined in a muffle furnace for 1 h at temperature ≤ 800°C. After heat treatment the agglomerated material was milled in order to obtain particles smaller than 160 μm in size, which comprised aggregates of nanosize particles. X-ray phase analysis and IR spectroscopy established that the synthetic material contained predominately hydroxyapatite, β-tricalciumphosphate, and a comparatively small amount of phases of the type calcium tetra- and orthophosphate.

The thin-layer ceramic membrane samples were obtained by centrifuging the slip, slip casting, plastic formation, and semi-dry pressing, which were optimized taking account of the physical-chemical as well as rheological properties and particularities of the hydroaluminosilicate and calcium-phosphate materials used [2, 3].

Samples 2 – 4 mm thick and 43 – 44 mm in diameter were obtained by pressing under pressure 3 – 5 MPa a plastic paste consisting of spondilovaya clay with relative moisture content 20.2% with a holding period of 5 min and calcined at 1000°C. Semi-dry bilateral pressing under pressure 40 MPa was used to form samples with the same geometrical dimensions but with water-content of the spondilovaya clay up to 6%. In this manner, the methods listed above were used to obtain elastically stiff UZhM-1 membranes (Table 1).

The following technology was used to produce the ceramic membranes in order to regulate more accurately the porous structure of the membranes. Powders with particles no larger than 50 μm were used to prepare a plastic ceramic paste, which was pressed under pressure ≤ 5 MPa and them dried slowly in the die to moisture content 4 – 5%, and then pressed again under pressure 35 – 40 MPa and calcined at 1000°C with a holding time of at least 1 h.

To convert the calcined ceramic samples into semi-permeable diaphragms, the samples were modified by colmatage of the pore channels using a water dispersion of bentonite with particle size ≤ 0.1 μm. The water dispersion, obtained by elutriation of the suspension in the presence of a peptizing agent — sodium tripolyphosphate $(Na_3PO_4)_n \cdot mH_2O$, contained 2% bentonite. The colmatage saturation of the pore channels of the ceramic by highly disperse bentonite particles was conducted under pressure 0.1 MPa with the sediment removed from the surface with the filtration process slowing to 1 drop in 10 min. The bentonite saturated samples were dried at temperature 105°C and calcined once again at temperature ≤ 1050°C. This made it possible to form an intermediate- or capillary-porous membrane UZhM-1m whose structure had a uniform density (see Table 1). The filtration parameters were determined using distilled water and a colloidal solution containing 0.1% bentonite.

Semi-dry pressing of powders and casting of suspensions were used to make UZhM-2 elastically stiff ceramic membranes with the same dimensions based on calcium-phosphate compounds. Powders of synthetic calcium-phosphate materials with moisture content ≤ 5%, particle size less than

[2] Here and below: mass content.

160 μm and bentonite particle size ≤ 50 μm, were used for semi-dry pressing. A mixture of powders of calcium phosphates with bentonite was pressed under pressure 90 – 100 MPa with a holding time of about 30 sec and calcined at temperature ≤ 800°C with holding time 1 h.

An unconventional procedure was used to check the structural nonuniformity of the UZhM-1m and UZhM-2 membranes and to check the associated density nonuniformity. For this, a membrane tested for boiling over 2 h and then dried at 150°C was cooled in an exciccator, covered its lateral surface with water repelling agent such as polyethylsiloxane, after which the coating deposited was thermally fixed at 180°C in 2 h. The prepared membrane was placed into a Petri dish on several conical supports and covered with distilled water to contact with the bottom surface of the sample. The water level was adjusted to mid-height of the sample and maintained until the experiment was completed. Next, the open surface of the sample was observed, recording the time at which the wet sections appeared and the number and area of such sections with the help of a transparent measuring grid. The elapsed time up merging of the wet sections was measured. The alternation of dry – dense and wet – loose sections of the membranes attests to the nonuniformity of the porous structure.

The nonuniform distribution of the ceramic mass due to autohesion, i.e., decrease of the friability of the powders, when placed in the die, and also because of the accompanying nonuniform distribution of the load in individual sections of the mass being shaped by pressing, and differences between their moisture content give rise to structural nonuniformity, which can be viewed as a random variable which follows the laws of probability [4].

The function $F_m = \Phi(\tau)$, characterizing the dependence of the moist sections on the time factor, can be regarded as a random function among many such functions, and the derivative of this function characterizes the nonuniformity of the structure formed [4].

Least-squares processing of the experimental data gave analytical expressions for the function $F_m = \Phi(\tau)$ and its derivative $F_m^1 = f(\tau)$:

$$F_m = b_0 + 0.5 b_1 \tau;$$

$$F_m^1 = 0.5 b_1 \tau - 0.5,$$

where b_0 and b_1 are empirical constants which depend on the parameters of the model being tested; τ is the onset time of contact between the surface of the sample and the water.

The diameter of the samples with the dimensions indicated is much larger than the thickness. As a result, the density distribution over the cross section is nonuniform [5]. The nonuniformity of the structure can be checked additionally by means of gas-liquid porometry using the "gas bubble" method. One other improvement was made to the technology in order to obtain ceramic calcined elastically stiff membranes. A series of samples was made from a ceramic mass with the initial relative moisture content ≤ 17% under pressure ≥ 15 MPa with a holding time 5 min with the pressure gradually decreased to 5 MPa in 10 min. The blank was dried in 1.5 h in dies at 60°C with repeated pressing under pressure no higher than 35 MPa and 10% moisture content of the ceramic mass, which is optimal for semi-dry pressing. After 20 min the pressure was about 15 MPa. After the samples were calcined at 1000°C, hydrothermal treatment by boiling was applied. Distilled water was used to determine the uniformity of the structure and filtration properties of the membranes. The initial filtration rate under pressure 12 kPa of the matrices obtained in this manner was approximately 1.5 times greater than for model samples made by centrifuging a slip and standard plastic formation.

A water suspension of BHAp or its composite with 15% sodium-silicate glass was used to make non-calcined semipermeable elastically resilient membranes UÉM-1 and UÉM-2 (see Table 1) by slip casting. BHAp powder with particle size less than 50, 50 – 90, and 160 μm as well as polyvinyl alcohol powder as a high-molecular polymer binder (≤ 20% of the composition) were used. To improve the hydration and subsequent colloidization of the PVA, the water suspension obtained was heated in a water tank for 10 – 15 min, after which the prepared slip was poured onto a plastic substrate in a framework made of a chemically stable material. At the completion of the coagulation process and hydration hardening of the composition obtained (12 – 24 h after poring), the membrane was removed from the mold. To avoid plastic deformation, the membranes were additionally dried under a load at room temperature for 12 h.

The properties of the UÉM type membranes were investigated in accordance with the existing procedures, keeping in mind their practical purpose. The apparent and computed density, porosity, sorption power, and solubility in the model physiological solution (0.9% isotonic solution of NaCl) at temperature 36 – 37°C (experiments *in vitro*) were determined.

Cracks due to the separation of the components (as a result of their different density) were observed in the model samples of ceramic matrices based on spondilovaya clay which were calcined at 1000°C and obtained by centrifuging a slip with relative moisture content 26%. Their pore structure was found to be nonuniform, i.e., permeated by numerous capillaries of different shape, because of which the compression strength of the diaphragms was comparatively low, not exceeding 15 MPa.

The model samples of the matrices formed by pressing from plastic mass with relative moisture content ≥ 20% likewise possessed defective structural fragments with capillary channels with substantial cross sections (30 – 50 μm) and microcracks which appeared during drying. As a result, the strength of such samples of the ceramic matrices did not exceed 20 MPa.

TABLE 2.

Indicator	Elastically stiff membranes		Elastically resilient membranes	
	UZhM-1, UZhM-1m	UZhM-2	UÉM-1	UÉM-2
Volume shrinkage, %:				
on drying	8 – 11	–	12 – 15	8 – 11
on calcination	≤ 6.5	1.2 – 1.5	–	–
Thermal stability, °C	≤ 1000	≥ 850	≤ 150	≤ 150
Density, g/cm^3:				
computed	2.4 – 2.6	2.5 – 2.7	2.6 – 2.8	2.3 – 2.6
apparent	1.5 – 1.8	1.3 – 1.6	0.9 – 1.2	1.1 – 1.3
Maximum strength, MPa:				
compression	54 – 70	48 – 64	–	–
tensile	11 – 14	≤ 12	15 – 20	≤ 10
Relative elongation (with rupture), %	–	–	7 – 10	≤ 5
Porosity (total), %	31 – 42	37 – 48	50 – 63	45 – 58
Water absorption, %	21 – 29	≤ 17	–	–
Sorption capacity (for distilled water), g water/g dry material	–	–	1.2	0.8
Degree of swelling, %	–	–	> 150	≤ 130
Mass loss on boiling, %	0.6 – 1.0	≤ 1.2	Expand	
Solubility in a physiological solution (biostability), mg/(cm^2 · day)	–	–	0.73 – 0.80	≤ 0.85
Gas permeability, μm^2	$(1.7 – 2.5) \cdot 10^{-4}$	$(0.8 – 1.5) \cdot 10^{-4}$	Impermeable to gas	
Filtration rate (distilled water), dm^3/(m^2 · h)	≤ 50.0	31.6	Are resorbed	

The use of semi-dry pressing to produce the ceramic samples UZhM-1 makes it possible to reduce these drawbacks to a minimum, but for low pressing pressures the structure formed still is observed to have some nonuniformity, which is expressed as a considerable difference between the total and open porosity. The main physical – mechanical properties of the elastically stiff and elastically resilient thin-layer ceramic membranes are presented in Table 2.

The appearance of a density difference in flat thin-layer membranes UZhM-1 is due to the mobility of the almost dry press powders used for hydroaluminosilicates and the ratio of the diameter to the thickness of the samples formed. The surface area of the compacts which receives the pressing pressure and the ratio of the height of the compacts, which is responsible for the redistribution of the load, is 1 : 0.15 or 1 : 0.09. Such a ratio increases the nonuniformity of the density distribution over filtering surface [5].

For semi-dry pressing, aside from the "form factor" of the ceramic membranes, the friability and the formability of the press powders, which depend on the size, degree of isometry, and surface character of the micrograins, affect the density nonuniformity of the ceramic membranes. For a substantial content of fractions smaller than 0.1 mm and elevated moisture content, which increase the coupling of the micrograins, the press-powder friability decreases. An increase of the size, density, and stiffness of the grains impedes the formation of the compacts and results in excess "graininess" of the structure of the membranes, which has a negative effect on the technical properties of the finished ceramic [5, 6]. Isometric grains with a comparatively smooth surface give high friability and packing density. Angular and nonisometric press-powder grains can increase the internal coupling forces in the pressed samples.

The effect of these factors was taken into account and reduced to a minimum, in the course of improving the technology for fabricating UZhM-1m membranes, by colmatage of the ceramic with high-dispersity bentonite and optimizing the pressing of the initial powders. Tests for structural uniformity of the UZhM-1m membranes indicate that the effective area and initial filtration rate are higher than for UZhM-1 membranes because of the absence of extremely dense sections as a result of the more uniform distribution of the pore channels over the effective radii.

The UZhM-2 membranes, which are based on the synthetic calcium – phosphate materials and bentonite and were obtained similarly to the UZhM-1 and UZhM-1m membranes but with a lower calcination temperature, possess close values of the total porosity and mechanical strength (see Table 2). The membranes UZhM-2 have a somewhat worse gas permeability and filtration rate for distilled water. This is due to the decrease of the water absorption as a result of the substantial fraction of the closed porosity of cal-

cium-phosphate materials and the special structure of the pores in the micrograins [2].

The UÉM-1 and UÉM-2 membranes are bioactive ceramics with prolonged solubility, which is required for biomaterials. The sorption capacity of these membranes with respect to distilled water is close and lies in the range 0.8 – 1.2 g water/g dry material. The swelling of the membranes in distilled water and a physiological solution at 37°C reaches comparable values. In vitro tests of these membranes attest to the comparatively small difference of solubility between them. However, the highest values of this important parameter for the UÉM-2 membranes reach 1.32 %/cm^2 per day, which is due to the presence of the composite BHAp – glass in them. The glass phase present in UÉM-2 membranes somewhat decreases tensile strength and relative elongation of the membranes as compared with the analogous parameters of UÉM-1 membranes. These parameters determine the great promise of elastically resilient membranes based on BHap as periodontal membranes used in stomatology.

In summary, ceramic elastically stiff and elastically resilient capillary-porous structures have been obtained and the possibility of modifying them into thin-layer semi-permeable membranes with filtration properties has been investigated. The most effective technological methods of fabricating special-purpose ceramic membranes based on spondilovaya clay and calcium-phosphate materials are semi-dry pressing of the initial powders and casting from suspensions.

The technological methods of forming capillary-porous ceramic structures have been optimized taking account of the physical – chemical and rheological properties as well as the particularities of the materials used. The appreciable decrease of the density nonuniformity of their filtering surface has confirmed the effectiveness of the proposed technology for pressing a charge to obtain ceramic elastically stiff matrices.

Ceramic elastically stiff matrices based on hydroxyapatite possess somewhat lower gas permeability as compared with matrices based on spondilovaya clay, but this does not decrease the prospects for using them as semi-permeable ceramic membranes used for filtration purification.

Polyvinyl alcohol used as a polymer binder to make resorbable non-calcined membranes imparts elastic resilience to them. Elastically resilient membranes based on biogenic hydroxyapatite manifest adequate biostability in a physiological solution, and for this reason they can be used as periodontal membranes.

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